Low surface area nanosilica from an agricultural biomass for fabrication of dental nanocomposites

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Abstract

This study aimed to obtain nanosilica with desirable characteristics from an agricultural biomass waste using an organic acid. The effect of the feed rate of the precipitant and the mixing speed on the morphology and characteristics of nanosilica from rice husk for use as fillers in dental nanocomposites has been explored. The feed rate showed considerable effects on the agglomeration and the size of the silica nanoparticles. At a feed rate of 0.2 ml/min, the particles were bigger and highly agglomerated with a mean particle size of 261 nm. The mean particle sizes for the feed rates of 1 ml/min and 5 ml/min were 213 nm and 174 nm, respectively, exhibiting a decrease in the mean particle size with increasing feed rate. The shape of the silica nanoparticles depended on the mixing speed and it was possible to obtain spherical, dense, low surface area silica particles suitable for use in the fabrication of dental nanocomposites using this simple technique.

1. Introduction

Rice husk, a milling byproduct of rice, is an agricultural waste which is usually burnt in the open air or stacked on farmland, releasing large amounts of hazardous substances, occupying land resources, and polluting the environment [1]. It has a characteristic of hard surface, high silica content, small bulk density, not easily decomposed by bacteria and has traditionally been disposed in landfill. This can result in a source of pollution, eutrophication and perturbations in the aquatic and terrestrial life [2]. When used to generate electric power, the emission of rice husk ash into the ecosystem is associated with its persistent, carcinogenic and bio-accumulative effects, resulting in silicosis syndrome, fatigue, shortness of breath, loss of appetite and respiratory failure [3].

Rice husk was thought to be of no commercial value, but the silica in rice husk which is highly porous with light weight and high surface area has made it economically important [4]. Moreover, the commonly used raw materials used in the classic sol–gel method are relatively expensive [5]. The content of amorphous silica in rice husk is the highest in all gramineae plants [6] and several authors have concluded that rice husk is an excellent source of high grade amorphous silica [7–9].

Amorphous silica powder is a basic raw material that is widely used in industries associated with ceramics, rubber, electronics, catalysis, pharmaceutics, dental materials and other materials [10]. One application where the silica obtained from rice husk could be put into use is as fillers in dental composites which have not been studied widely. The dental composites available currently in the market use commercially prepared silica which greatly increases its cost due to the high cost of the precursors involved in its production. Hence, it would be useful if a relatively inexpensive source of fillers could be explored resulting in reduced cost.

The properties of dental composites are highly dependent on the characteristics of the fillers, like the shape, size, surface

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area and porosity. For example, a positive effect of the presence of nanofiller particles was observed by an improvement in flexural strength, surface hardness and fracture toughness [11]. Also, a combination of mesoporous and nonporous materials can be used to prepare stronger dental materials that may resist hydrolysis and wear [12]. Hence, the current study aimed to look into the manipulation of the morphology of the silica particles so that it could be used as fillers in dental nanocomposites.

Previous researches have mainly concentrated on obtaining silica with a high surface area [13,14]. Studies have shown that fillers with low surface area are favorable when used to fabricate dental composites. The larger surface area to volume ratio of the fillers has shown to increase water uptake resulting in the degradation of filler/matrix interface [15]. Moreover, a higher surface area also causes a reduction in the filler loading which is disadvantageous [12]. Several researchers have shown that filler loading reduces as a consequence of a high surface area to volume ratio, thereby limiting mechanical properties [16,17]. However, the inclusion of nanoclusters in the nanofilled material provided distinct mechanical and physical properties compared with those of the microhybrid resin based composites [15]. Therefore, fillers with lower surface area are preferable. The present study therefore intended to obtain silica with a low surface area ideal to be used in the fabrication of dental nanocomposites.

Studies have shown that spherical shaped fillers have a positive effect on the properties of the dental composites because spherical equiaxial fillers are free from entanglement and can be better dispersed in the matrix [18]. Composites with spherical filler particles are shown to exhibit lower shrinkage-stress values as compared to those with irregular filler particles. This is due to an increase in the ability of the dispersed phase to move within the matrix and relax stress, with increasing sphericity [19].

Deriving silica from rice husk has been extensively reported in the last two decades, but none has focused on obtaining silica ideal for use as fillers in dental composites. It is reported that active silica with a high specific area could be produced from rice husk ash after heat-treating at 973 K in air [20]. Moreover, it has been reported that the fungus *Fusarium oxysporum* rapidly biotransforms amorphous plant biosilica into crystalline silica and leach out silica extracellularly at room temperature in the form of 2–6 nm quasi-spherical, highly crystalline silica nanoparticles [8]. Mixed-phase bimodal mesoporous silicas (BMS) was synthesized by a simple sol–gel technique using rice husk ash-derived sodium silicate as a silica source [14]. A consecutive preparation of D-xylose and superfine silica from rice husk was also carried out [6]. Rice husk ash was treated with acid leaching and then boiled with base to leach silica [21]. Amorphous silica was successfully extracted at a 90.8% yield through base dissolution–acid precipitation of rice straw ash generated by a three-stage heating process [22]. A recyclable technology for preparation of silica powder using rice husk ash and NH_4F has also been proposed [23]. The current study employs a simple method to obtain spherical nanosilica particles.

Several researchers have looked into several aspects of the processing conditions on the morphology and characteristics of silica particles from rice husk. Previous studies have shown that it is possible to manipulate the morphology and characteristics of the silica particles by simple alterations in the extraction process. A study on the effects of calcination parameters, including temperature and time, on the silica phase of original and leached rice husk ash using X-ray diffraction (XRD) analysis showed the presence of totally crystalline silica in the original rice husk ash prepared at 800 °C but not in the leached rice husk ash [24]. They suggested that the leaching procedure, low calcination temperature and short calcination time to prepare more active amorphous silica from the rice husk. High purity of the silica gel has been found to be dependent on the reflux time and water loading by the addition of boiling deionized water to the silica gel prior to titration with 1 M H_2SO_4 [10]. A study utilized rice husk as an alternative silica source for the synthesis of MCM-22 showed that the duration required for zeolite crystallization was significantly decreased under varying-temperature conditions [25]. It was shown that the morphology of the silica particles from rice husk was dependent on several parameters like sodium silicate concentration, addition of solvent, pH, calcination temperature, etc. [26,27]. Although innumerable studies have been carried out taking into account different methods of utilizing rice husk in general and on obtaining amorphous silica in particular, there is no report looking into the effect of feed rate on the obtained silica particles to the best of our knowledge. In this study, the effect of the above mentioned parameters on the morphology and characteristics of nanosilica from rice husk with a proposal to use it as fillers in dental composites is reported.

2. Materials and methods

2.1. Materials

The rice husk was obtained from a local rice mill in Pak Badol, Kelantan, Malaysia. Sodium hydroxide (NaOH), hydrochloric acid (HCl) and 2-propanol were obtained from Merck (Germany). HCl was used in diluted form to remove the metallic impurities from the rice husk. All other chemicals were used without further purification. Deionized water was used wherever applicable.

2.2. Preparations

2.2.1. Extraction of silica from rice husk

Rice husks were washed thoroughly with water to remove the soluble particles and dust or other contaminants such as heavy impurities. They were then dried overnight in a hot air oven at 110 °C. The dried rice husks were heated in an acidic solution (1 M solution of HCl in a hot water bath) at 75 °C for 90 min to remove metallic impurities. The husks were thoroughly washed several times with deionized water. The wet solid was subsequently dried overnight in a hot air oven at 110 °C. The rice husks were heated in a 10% solution

of NaOH at 90 °C for 1 h and filtered to obtain sodium silicate solution (SSS). The filtrate was used as the source for nanosilica.

2.2.2. Precipitation of silica by different techniques

The nanosilica was obtained by precipitating SSS with an organic acid solution with constant stirring until the pH dropped to 8. A pH of 8 was used with the aim of obtaining low specific surface area, dense silica that could be suitable for use as fillers in dental composites. The SSS used was diluted with deionized water at a ratio of 1:0.7. Prior to precipitation, 20 ml of propanol was added to the SSS H_2O mixture. As the pH dropped to 8, the precipitation was stopped and the gel was further stirred for another 45 min. The gel was washed several times and centrifuged at 4000 rpm for 5 min with each wash in order to obtain an acid free white precipitate. The white precipitate was calcined at 500 °C for 30 min in a muffle furnace to obtain pure white silica powder. The silica particles were characterized using several techniques.

The effect of two variables on the characteristics of the silica particles were studied, namely, mixing speed and feed rate of the precipitant. To study the effect of mixing speed, an overhead stirrer (RW20 digital Overhead stirrer, Fisher Scientific, USA) was used and three different speeds of mixing during precipitation were studied. To study the feed rate, three different rates of feeding the precipitant (0.2 ml/min, 1 ml/min and 5 ml/min), using a buret were studied.
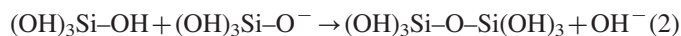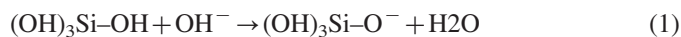
2.3. Characterization

The silica particle morphology was characterized using a Transmission Electron Microscope (Philips Electron Optics, Eindhoven, The Netherlands). Image analysis was done using Olympus 'Cellsens' – Soft Imaging Solution GmbH, Munster (Germany). Fourier transform infrared spectroscopy (FTIR) experiments were carried out on a Spectrum 100 Optica FTIR spectrometer (Perkin Elmer, USA) employing the KBr pellet method. The specific surface area of the silica samples was measured by N_2 adsorption at 77 K using the Brunauer Emmett Teller (BET) method (Quantachrome Instruments v2.02, USA).

3. Results and discussion

3.1. Extraction and general characterization of the silica particles

Different authors have used different methods and different precipitating acids for the extraction of silica from rice husk [8,14,20]. Some researchers used ortho-phosphoric acid [5,27,28], while others have used nitric acid [29], sulfuric acid [22] and hydrochloric acid [30] for the precipitation of sodium silicate. In the current study, a weak acid was used instead of strong acids, which has not been reported by earlier researchers. When the organic acid was used as the precipitant, gelation started as the pH of the sodium silicate solution decreased. During gel formation, a poly-condensation reaction may occur in the following two consecutive paths [30].

$$(OH)_3Si–OH + OH^- \rightarrow (OH)_3Si–O^- + H2O \tag{1}$$

$$(OH)_3Si–OH + (OH)_3Si–O^- \rightarrow (OH)_3Si–O–Si(OH)_3 + OH^- \tag{2}$$

Different authors have studied the effect of different pH values on the characteristics of the silica obtained. In a recent study, high specific surface area (1018 m^2/g) silica was obtained using a pH of 3.2. It was suggested that decreasing the pH increased the specific surface area, total pore volume, micropore volume, mesopore volume and pore diameter [28]. Therefore, a constant pH of 8 was used in this study. The shape and degree of agglomeration of the silica nanoparticles varied depending on the feed rate and the mixing speed. The parameters were manipulated to obtain silica particles suitable for use as fillers in dental nanocomposites.

Fig. 1 shows the infrared spectra of the silica obtained from rice husk, which was examined by FTIR in the range of 4000–500 cm^{-1} and is typical of silica. The peak at 471 cm^{-1} corresponds to the siloxane (Si–O–Si) bond, the peak at 803 cm^{-1} corresponds to the Si–OH bond, and the peak at 1091 cm^{-1} corresponds to the Si–O bond. The adsorption peaks at 3448 cm^{-1} and 1638 cm^{-1} correspond to the H–O–H stretching and bending modes respectively.
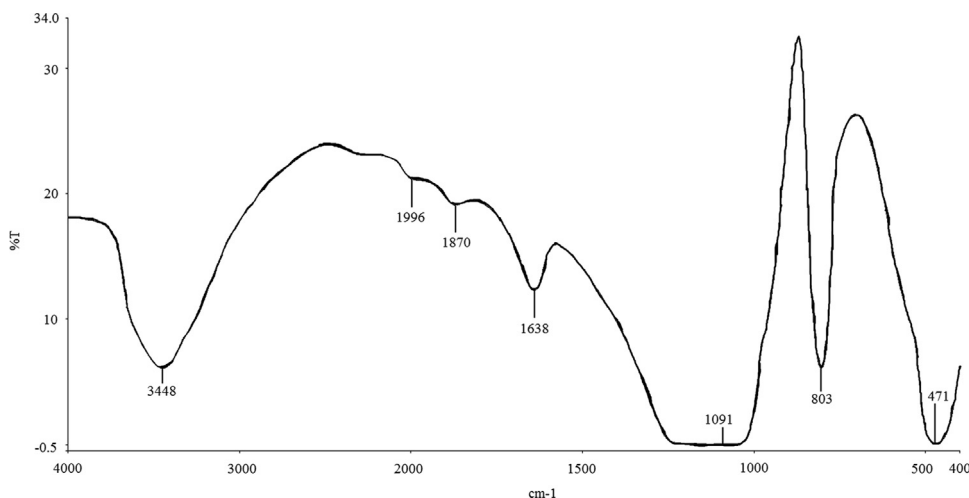

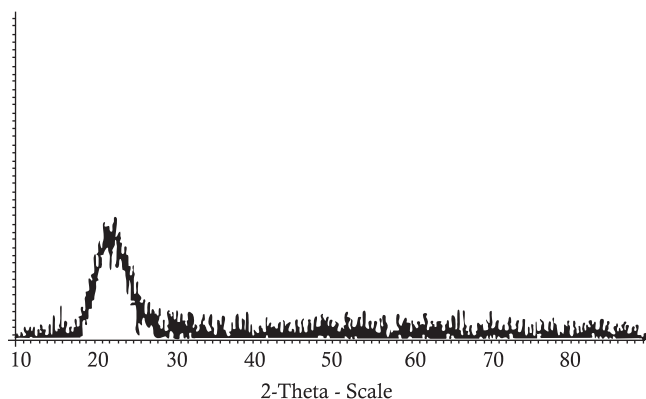Fig. 1. FTIR spectrum of the silica obtained from rice husk using the precipitation technique.

Fig. 2. X-ray diffraction pattern of the silica obtained from rice husk by precipitation technique using an organic acid and calcining at 500 °C.

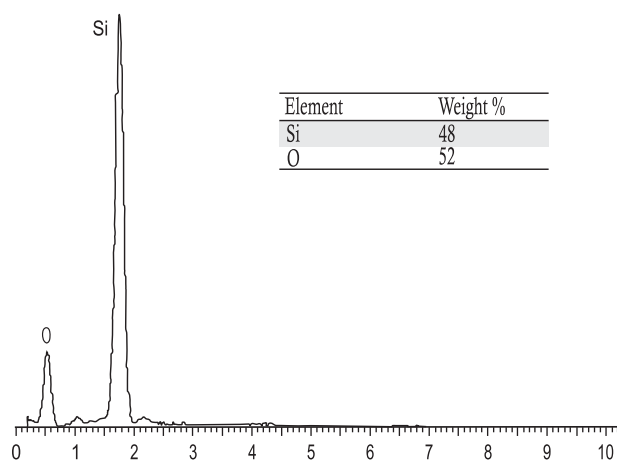| Element	Weight %
Si	48
O	52

Fig. 3. EDX spectrometric data of silica from rice husk by precipitation technique using an organic acid as the precipitating acid.

The X-ray diffraction pattern of silica powders as shown in Fig. 2 having a broad and high intensity peak at $2\theta = 22°$ suggests a typical amorphous structure which is further confirmed by the absence of sharp peaks. Since a calcination temperature of 500 °C was used, the nanosilica obtained was amorphous in nature, which is supported by other findings. It was reported that ash prepared at a temperature of about 500–600 °C consists of amorphous silica. At 800 °C, cristobalite was detected, and after burning at 1150 °C, both cristobalite and tridymite were present [31]. Silica in rice husk ash can remain in amorphous form at combustion temperatures of up to 900 °C if the combustion time is less than 1 h, whereas crystalline silica is produced at 1000 °C with combustion time greater than 5 min [32]. EDX analysis as shown in Fig. 3 detected the presence of silicon (Si) and oxygen (O) due to the formation of siloxane bond (Si–O–Si) and silanol group (Si–OH) with no other impurities.

3.2. The effect of feed rate

The use of the sol–gel method to synthesize silica showed that the feed rate of ammonia into the reaction mixture has significant effect on particle size, size distribution and yield [33]. Slower feed rate resulted in smaller particle size with narrow standard deviation (SD), while faster feed rate resulted in larger particles with wider SD. Silica nanoparticles were prepared using a semi-batch process, to study the effect of several parameters including the feed rate of reactant on the size of the silica particles and it was concluded that the particle size decreased with an increase in the feed rate of reactant and reaction temperature. SD of SiO_2 particles was shown to decrease with reduction of the feed rate and increasing the reaction temperature [34]. In the current study, the particle size decreased with an increase in the feed rate of the precipitant. A slow feed rate probably allowed more time for the primary particles to aggregate, resulting in larger particles.

The feed rate of the precipitating acid showed a marked effect on the degree of agglomeration, particle shape as well as the particle size. A slow feed rate of 0.2 ml/min produced silica particles that were highly agglomerated (Fig. 4), whereas, a high feed rate (5 ml/min) produced a considerably reduced degree of agglomeration, with both spherical and non-spherical shaped silica particles. A medium feed rate of 1 ml/min produced perfect spherical silica particles with considerably less agglomeration. The minimum, maximum and average particle size decreased with an increase in the feed rate as shown in Table 1. There was no feed rate dependent increase or decrease of surface area or pore diameter of the silica particles.

3.3. Effect of mixing speed

Although perusal of literature showed no work on the effect of mixing speed on the resultant silica particles, there have been studies focusing on the mixing mode and mixing sequence. A unique mixed-phase BMS with uniformly infiltrated SBA-3-like in SBA-15 was synthesized by modifying the mixing sequences of the starting materials [14]. It was shown that the particle agglomeration of the silica obtained via the sol–gel synthesis was stronger with magnetic agitation compared to ultrasonication [33].

Fig. 5 shows the effect of mixing speed on the morphology of the silica nanoparticles. It has to be noted that the feed rate was kept constant at 5 ml/min. At a speed of 1000 rpm, the particles were a mixture of spherical and non-spherical in shape. At a lower speed of 750 rpm, the particles were a mixture of spherical and agglomerates. At a speed of 500 rpm, the silica particles were more spherical and less agglomerated. It has been envisaged to further explore the effect of mixing speed by deferring the feed rates as it is expected to affect the morphology of the particles. The particle size distribution graph (Fig. 6) shows that it is uniformly distributed at all mixing speeds studied. At 1000 rpm, the silica nanoparticles showed a narrow particle size distribution in comparison to the other mixing speeds. The particles that were spherical in shape have only been measured for particle size determination.

3.4. Surface area and pore characteristics

Based on the TEM images, it was decided to analyze the BET surface area and the pore characteristics only for the silica obtained with varying feed rates at a speed of 1000 rpm. Fig. 7a–d shows
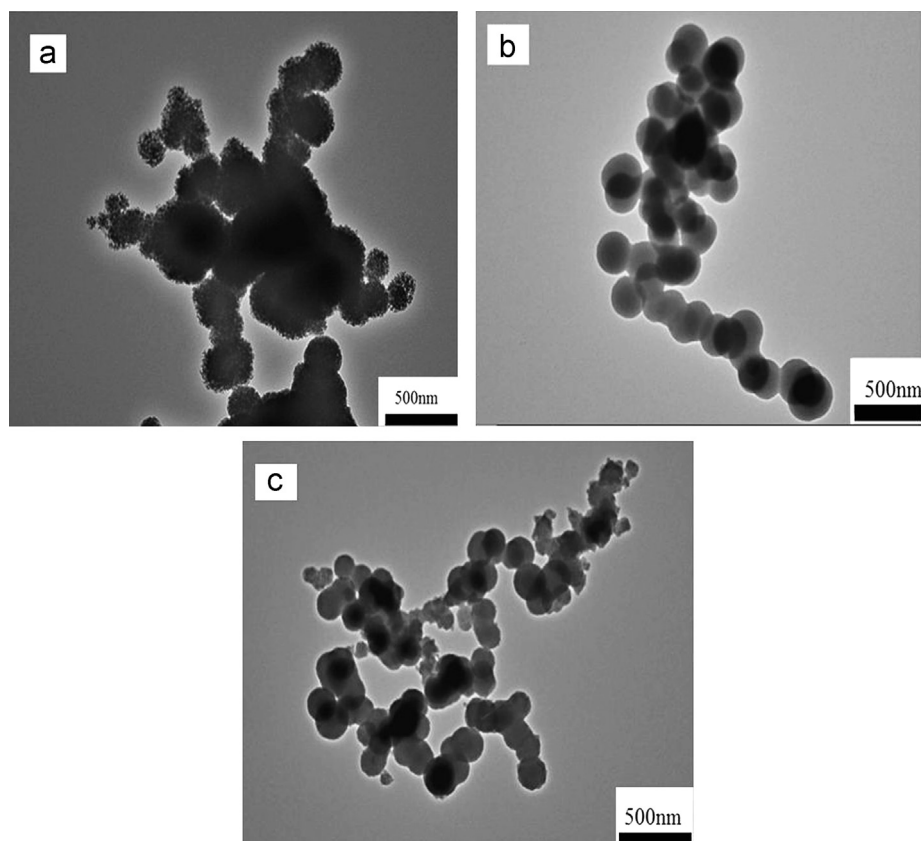
Fig. 4. TEM images showing the effect of feed rate of the precipitant on the morphology and particle size of silica (scale bar=500 nm): (a) feed rate of 0.2 ml/min, (b) feed rate of 1 ml/min and (c) feed rate of 5 ml/min.

Table 1
Effect of feed rate on the surface area and pore characteristics of silica powders by BET and BJH calculation from nitrogen adsorption–desorption isotherm.

Sample	BET surface area (m²/g)	Average pore diameter (nm)	Particle size (nm)	
			Range	Mean
0.2 ml/min, 1000 rpm	10.8	24	87–525	261
1 ml/min, 1000 rpm	7.4	33	54–414	213
5 ml/min, 1000 rpm	15	27	43–316	174

the isotherm curves of silica samples obtained from rice husk using different feed rates. Convexity towards the relative pressure axis characterizes these isotherms. However, a hysteresis loop appears between the adsorption and desorption branches, indicating capillary condensation of the porous structure. All the isotherms belonged to the type II category based on the IUPAC classification, with H3 hysteresis loop. Type II isotherm represents unrestricted monolayer–multilayer adsorption and shows that the adsorbents are non-porous or macroporous. These results are consistent with BET surface area results and TEM observations as shown in Fig. 4. The type H3 loop, which does not exhibit any limiting adsorption at high p/pᵒ, is observed with aggregates of plate-like particles giving rise to slit-shaped pores [35]. The figure shows that the volume

adsorbed from sample produced by different feed rates increased according to the sequence of 1 ml/min, 1000 rpm (0.061 cc g^{-1}) < 0.2 ml/min, 1000 rpm (0.067 cc g^{-1}) < 5 ml/min, 1000 rpm (0.1 cc g^{-1}). Pore volume reduction according to the above sequence may result from the blocking of the pores by a larger metal salt present in the gel matrix due to the effect of mixing speed. The results for specific surface area, average pore diameter and particle size ranges are summarized in Table 1.

Fig. 8 shows the pore size distribution of silica samples produced by different feed rates estimated by the BJH model. The pore size distribution is the distribution of the pore volume with respect to pore size which is affected by the shape of the pores. Table 1 shows that the pore size distribution of the silica obtained using different mixing speeds are close to each other. Fig. 8 shows a narrowly distributed curve for the parameters 5 ml/min at 1000 rpm and 0.2 ml/min at 1000 rpm which may be due to the instability of the spherical shape of the silica particles (Fig. 4a and c) compared to the broad curve shown by 1 ml/min at 1000 rpm which could be due to the uniform particulate nature and spherical shape of the silica particles (Fig. 4b) [27,30].

3.5. Fillers for dental nanocomposites

Nanosilica has been used either alone, or in combination with other materials, as fillers in several commercial dental composites. Filtek Supreme Body uses a combination of
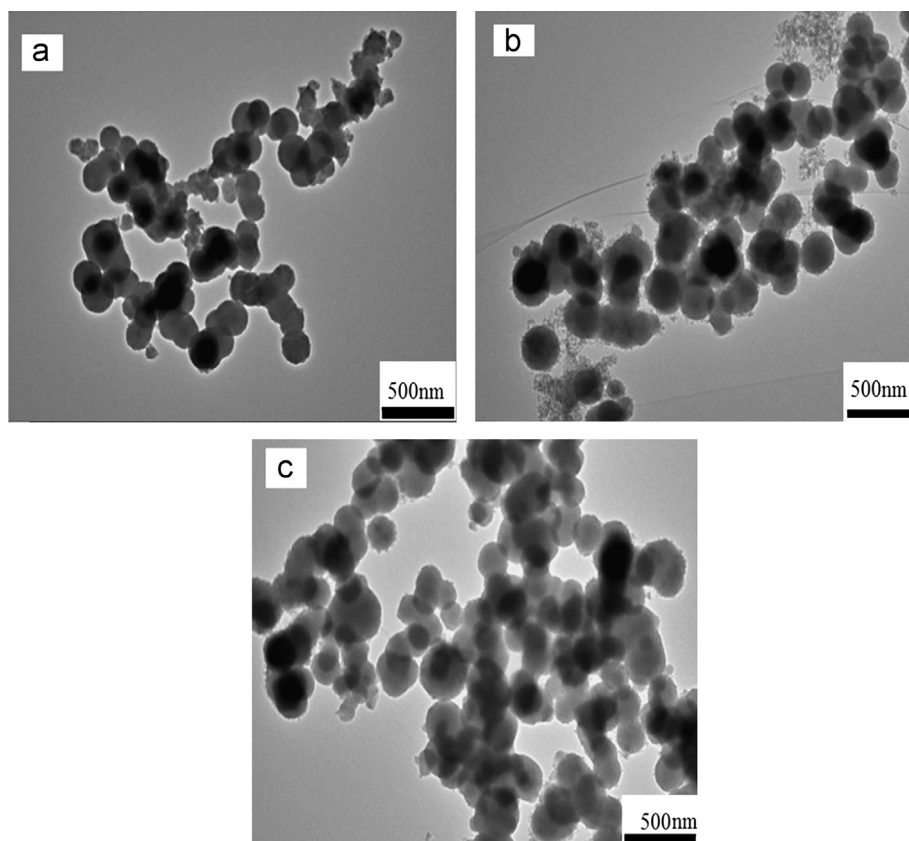
Fig. 5. TEM images showing the effect of mixing speed on the morphology and particle size of silica (scale bar=500 nm): (a) 1000 rpm (b) 750 rpm and (c) 500 rpm.
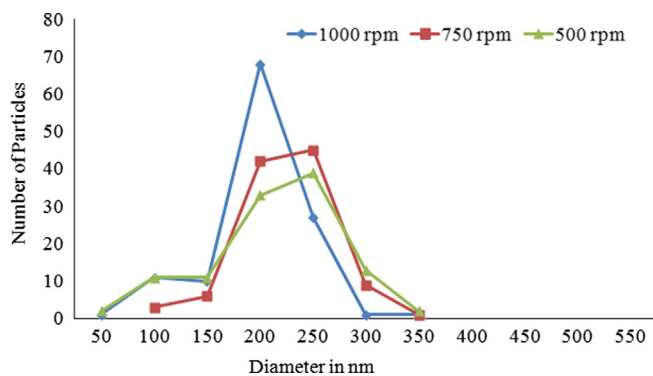

Fig. 6. Effect of mixing speed on the particle size distribution of silica. Feed rate of precipitant was 5 ml/min for all mixing speeds.

5–20 nm silica nanoparticles and 0.6–1.4 μm zirconia/silica nanoclusters. Filtek™ Z350 XT uses a combination of non-agglomerated/non-aggregated 20 nm silica filler, non-agglomerated/non-aggregated 4–11 nm zirconia filler, and aggregated zirconia/silica cluster filler with an average size of 0.6–20 μm (3M ESPE Dental Products, St Paul, MN, USA). Grandio and Grandio Flow (VOCO, Cuxhaven, Germany) also use nanosilica (20–60 nm) as fillers.

At present, to our knowledge, all nanosilica fillers used in dental composites are prepared using commercially prepared silica mostly using the sol–gel method. For example, 3M ESPE manufactures many of its fillers using the sol–gel

process wherein, fillers are made from liquid precursors, or a 'sol.', that are chemically and mechanically processed to produce particles (3M ESPE Dental Products, USA). In the current study, spherical nanosilica with a size range of 43–525 nm has been obtained from rice husk using a simple precipitation process. Even though the small particle size is important, other factors like the surface area of the filler also affect the mechanical properties of the dental composites. In the current study, it was possible to obtain nanosilica with a surface area ≤ 15 m^2/g, suitable for use as fillers in dental composites. It was reported that after certain loading, fillers with high surface area produced a composite mixture that was sandy or powdery, thereby limiting the filler loading. Using a combination of mesoporous and nonporous spherical (low surface area) fillers (500 nm diameter) allowed an increased filler loading, resulting in better mechanical properties [12]. In order to overcome the problems associated with fillers with high surface area, silica particles were thermally sintered at 1300 °C to obtain fillers with a low surface area (8.4 m^2/g). The experimental composites containing the sintered nanoparticles exhibited better mechanical properties in comparison to the microfilled composite [36].

The spherical shape and the variation of the particle size are other factors that could influence the properties of the dental composite with several reports of improvement in the properties. The silica particles obtained in the current study are dense and spherical in shape. At a feed rate of 1 ml/min, the silica
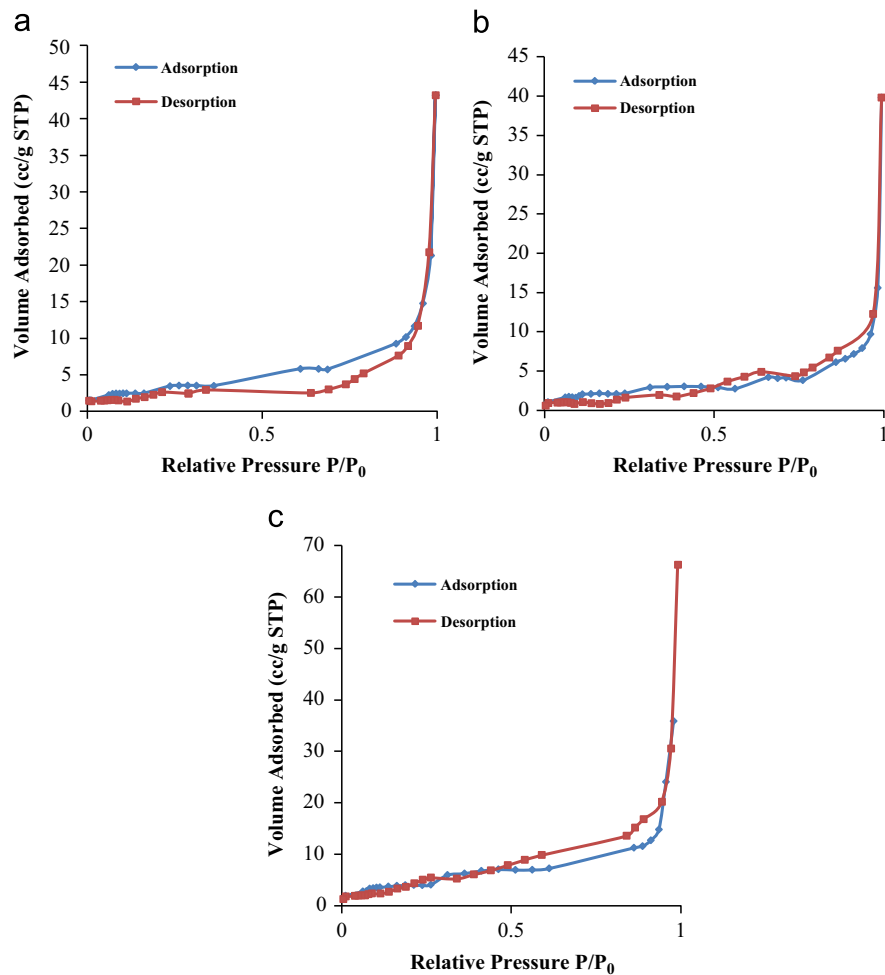
Fig. 7. The N$_2$ adsorption/desorption isotherms of silica particles using different feed rates: (a) 0.2 ml/min at 1000 rpm, (b) 1 ml/min at 1000 rpm and (c) 5 ml/min at 1000 rpm.
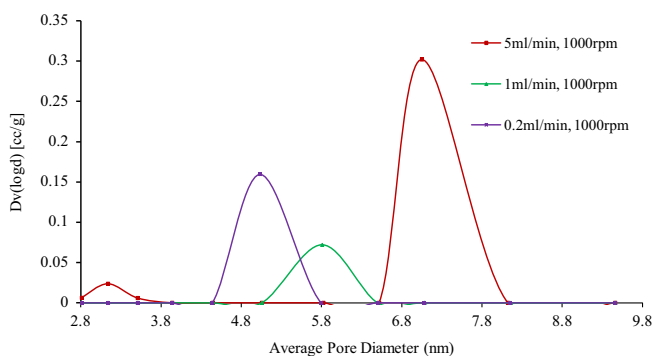

Fig. 8. BJH pore size distribution curves from the adsorption isotherm of various silica samples prepared at various feed rates at 1000 rpm.

particles are perfectly spherical in shape with a size range of 54–414 nm. Several commercial dental composites used hybrid or nano-hybrid particles to improve properties. For example, Filtek Supreme XT uses a combination of silica nanofiller and zirconia/silica nanocluster and Filtek Z-250 uses zirconia and silica fillers with a size ranging from 0.01 to 3.5 µm (3M ESPE Dental Products, USA). It has been shown that since mechanical stresses tend to concentrate on the angles and protuberances of irregular-shaped filler particles, the spherical shape of the fillers allows increased filler load and also enhances the fracture strength of the composites [37]. The spherical shape, especially in a mixture of different sizes, further favors an increase in filler load. Moreover, a combination of relatively small and varied size fillers allows a more dense packing, which in turn increases the possible filler volume-fraction of the resin-composites [38]. In Filtek Supreme™, a high filler loading was achievable due to the wide particle distribution and the spherical shape of the filler particles, equaling physical and mechanical properties of microhybrid composites [39].

As discussed earlier, a spherical shape, varying sizes and a low surface area are favorable characteristics of fillers used in dental composites. The current study showed that a combination of both optimized parameters is important in the determination of the morphology of the silica particles. From the data obtained, it is opined that a medium feed rate of 1 ml/min at a speed of 1000 rpm is suitable in obtaining spherical, uniformly distributed particle size, and minimally agglomerated nanosilica with a low surface area from an agricultural biomass.

It could serve as a low cost replacement for the current fillers used in the fabrication of dental nanocomposites and at the same time solve the problem of environmental pollution caused by mass dumping or burning of rice husk.

4. Conclusions

A method of obtaining nanosilica from rice husk by a simple method using a weak organic acid as the precipitant and by varying the feed rate and the mixing speed is presented here. Mixing speed as well as feed rate of the precipitant affected the morphology of the silica particles. A feed rate of 1 ml/min at a mixing speed of 1000 rpm produced perfectly spherical minimally agglomerated silica nanoparticles. This holds promise on the use of silica nanoparticles obtained from rice husk as fillers in dental nanocomposites.

Acknowledgments

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